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PHOTOEXCITATION OF CARBON FULLERENES

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13. ABSTRACT *(Maximum 200 words)*

Photoexcitation processes in cold and thermal C60 and C70 molecules in the gas phase were studied. We set up a supersonic beam source of cold fullerenes and used it to measure the beam energies for helium and krypton as driving gas. We studied thermionic emission from fullerenes following multiphoton pumping using laser pulses of 20 ns, 1 ps, and 150 fs duration. The wavelength dependence for REMPI was investigated from 315 to 335 nm. Multiphoton fragmentation processes and ultrafast dynamics of fullerenes were investigated.

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STATEMENT OF THE PROBLEM

Interest in fullerenes and fullerenes that have been doped with atoms and molecules is based on the expectation that novel materials can be generated having tailored electronic and optical properties. Optical spectroscopy of isolated fullerenes is considered a most direct approach to studying the electronic properties of these new molecules. To date, endohedrals containing La, La_2, Pr, Pr_2, and Pr_3 have been demonstrated, and it is expected that these materials will become available in quantities sufficient for optical spectroscopy in the very near future.

This report describes a series of experiments on cold and hot C_{60} molecules to provide information needed for spectroscopic research on endohedral fullerenes.

SUMMARY OF MOST IMPORTANT RESULTS

We conducted photoexcitation experiments on cold and hot C_{60} molecules to provide the information needed for spectroscopic research on endohedral fullerenes. A cold molecular beam source based on a pulsed supersonic expansion of C_{60} vapor was set up. This source and a conventional effusive Knudsen cell source were used to study multiphoton absorption of fullerenes.

We investigated the effects of intermediate resonance states in multiphoton absorption. We also investigated the feasibility of pump-probe experiments by using two different color sources as well as time-delayed photon sources. In addition, we explored the response of C_{60} to photo-excitation by nanosecond, picosecond, and femtosecond light sources under conditions of low, intermediate, and very high intensity.

The temporal characteristics and beam energies obtained in the pulsed C_{60} source were measured, as well as the wavelength dependence for gas phase excitation to the electronic state of C_{60} near 3.8 eV. We characterized the fragment distribution following excitation at various wavelengths.

EXPERIMENTAL SETUP

The typical experimental setup, shown in Figure 1, consists of a molecular beam source, a laser interaction region, extraction and acceleration fields, and a field-free drift region. The time-of-flight selected ions are monitored with a pair of multichannel plates and a 50-ohm anode. Photon interaction occurs in region I, approximately halfway between electrodes 1 and 2, where one or two focused beams of laser light intersect the C_{60} stream. Ions that are formed as a result of photon excitation are accelerated out of the interaction region and are then allowed to travel through a field-free region to the detector.

SUPERSONIC FULLERENE SOURCE

The two main components of the cold C_{60} source are shown in detail in Figure 2. They are (1) an oven capable of holding up to 75 mg of C_{60} with a maximum attainable temperature exceeding 1000 K and (2) a pulsed nozzle that can operate at a repetition rate of over 50 Hz. The two are held together with thin support rods. The water-cooled, pulsed nozzle is thermally

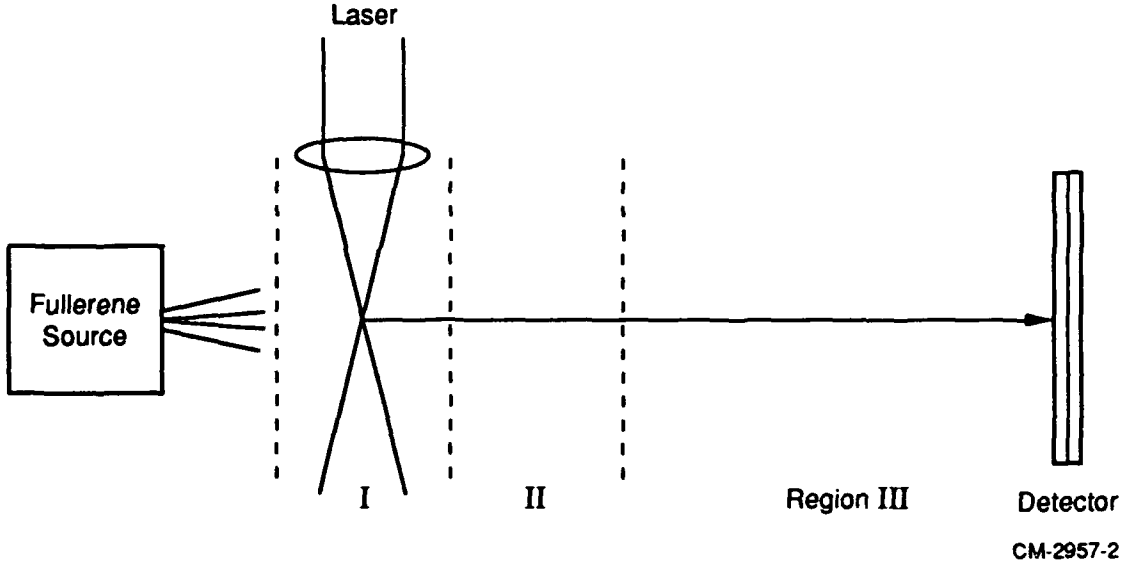
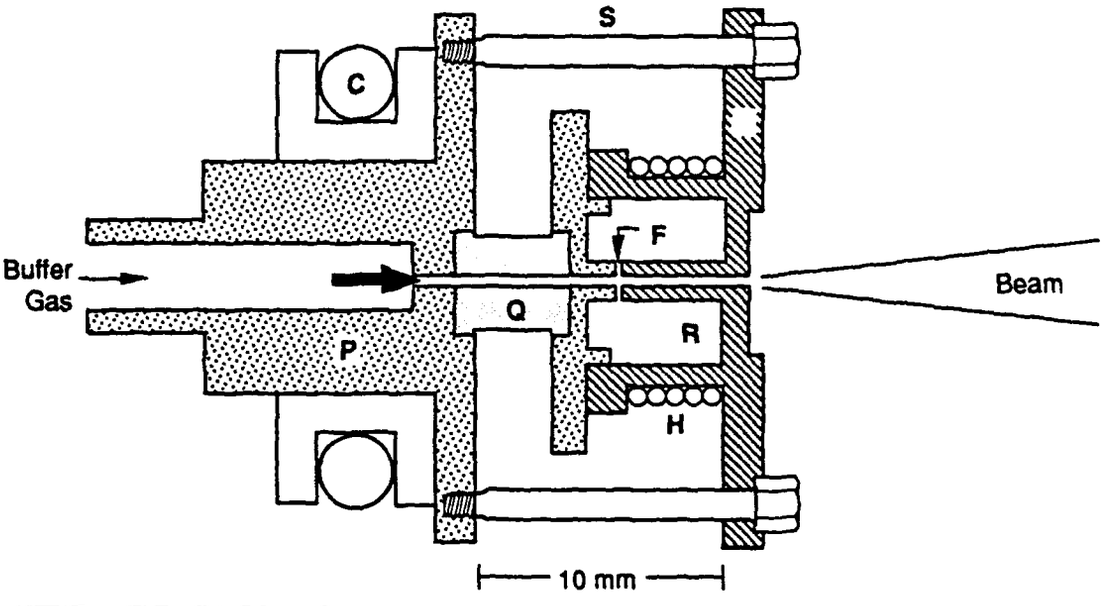


Figure 1. Schematic of experimental setup.



C Cooling Coil
H Heating Coils
P Pulsed Nozzle
Q Quartz Capillary
R Reservoir
S Support Rod
F Capillary Feed

CM-2957-1

Figure 2. High temperature pulsed molecular beam source.

Pulses of the buffer gas enter the capillary formed by the quartz tube, Q, and an axial hole in the reservoir, R. The buffer gas compresses and sweeps out the C_{60} vapor that accumulates in the capillary between pulses.

insulated from the oven by a quartz capillary. The nozzle uses a Teflon plunger and an electromagnet for its pulsed operation. The C_{60} oven is a cylindrical reservoir designed such that an axial hole acts as extension of the quartz capillary (1-mm inside diameter) and as the pathway for the driving gas emitted from the pulsed nozzle. Two radial channels, 250 μm in diameter, connect the inside of the C_{60} reservoir to the capillary. The oven is operated typically at 800 K, corresponding to a vapor pressure of C_{60} of about 2 mTorr. Rapid degradation of the C_{60} sample was observed to occur on a time scale of only a few minutes when the reservoir was heated to temperatures only slightly above 800 K.

CHARACTERIZATION OF BEAM SOURCE

The pulsed nozzle is synchronized with the laser, and it emits a stream of buffer gas (helium) into the quartz capillary from a reservoir held at 5 atmospheres. The helium pulse then enters the capillary of the assembly and sweeps out the C_{60} vapor that has accumulated in the capillary between consecutive gas pulses. Figure 3 shows the temporal characteristic of the C_{60} pulse emitted from the source as determined by photoionization by a pulsed laser beam of 15-ns duration. This plot was made by monitoring the magnitude of the C_{60}^+ signal as a function of the delay time between opening of the pulsed nozzle and the laser pulse. The temporal C_{60} profile shows a sharp peak of 20 μs FWHM about 360 μs after applying the electrical pulse to the valve. The sharp peak is followed by a broader peak (FWHM of 500 μs). The origin of the sharp peak is that, during consecutive laser pulses, the capillary is filled with C_{60} vapor from the cell. This vapor is compressed and pushed out of the capillary by the helium jet. After sweeping the capillary clean of fullerenes, the helium gas pulse continues, being fed by further C_{60} vapor from the oven.

Proof for this interpretation comes from a similar study using krypton as buffer gas. In the top of Figure 4 we show the temporal profile of C_{60}. The early peak in the profile is slightly broader than in helium but otherwise the profile is quite similar to that in Figure 3. In the krypton case, we have the possibility of monitoring the buffer gas directly by photoionization of the KrXe dimer, which is formed due to a small xenon impurity of the krypton sample. The temporal profile of KrXe (bottom of Figure 4) displays a broad peak only, in agreement with the mechanism for the formation of the compressed C_{60} peak discussed above. Dimer ion signals of C_{60} were observed to be very weak (<1% of C_{60} signal).

The velocities of the C_{60} beam in both krypton and helium buffer were measured making use of the time-delayed ionization process (see below). Because a significant portion of C_{60} that is multiphoton excited is observed to undergo delayed ionization, we can directly measure the speed of the C_{60} beam. To do this we reverse the electric field in region I thereby suppressing detection of ions that are formed immediately after the photon pulse. Under these conditions C_{60} molecules

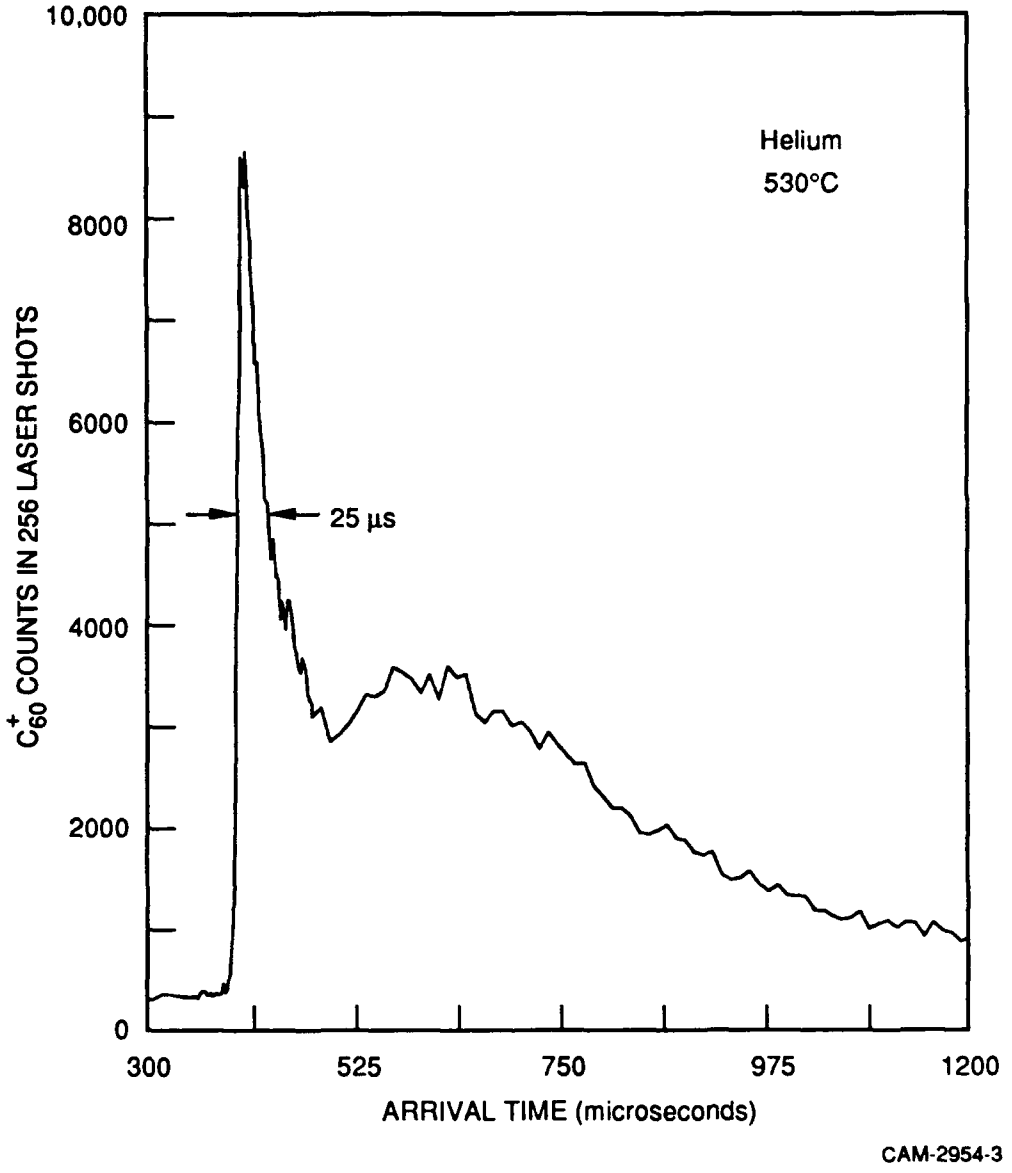


Figure 3. Temporal profile of compressed C_{60} pulse measured by multiphoton ionization 1 cm from the end of the capillary.

Helium is the buffer gas. The narrow peak corresponds to C_{60} molecules that accumulated in the capillary between pulses.

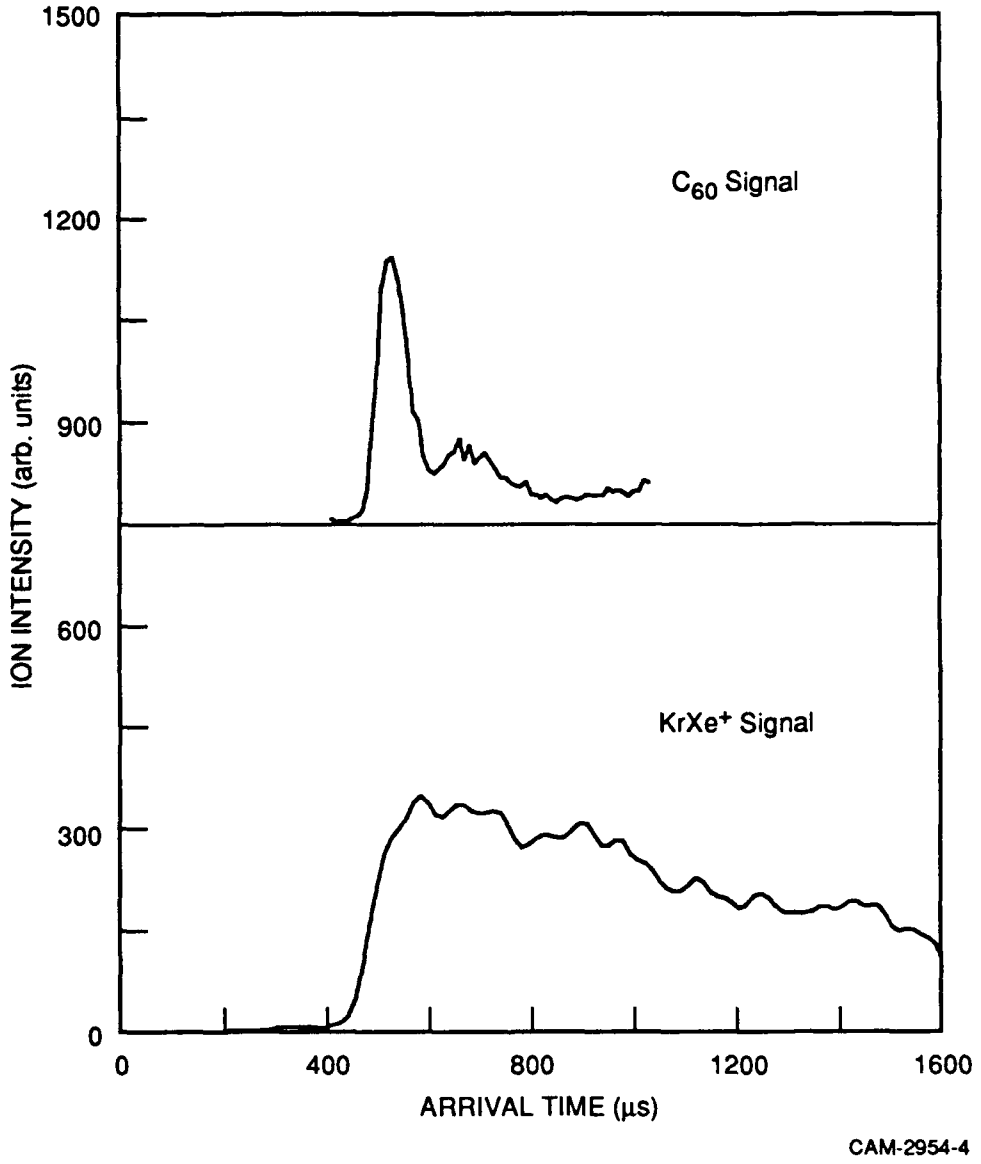


Figure 4. Comparison of temporal profiles of C60 and buffer gas.

Top: Temporal profile of compressed C_{60} using krypton as buffer gas.
Bottom: Temporal profile of buffer gas density.

that were multiphoton excited by did not ionize instantly drift with the characteristic beam velocity through region I. If an accelerating field is applied in region II, then C_{60} molecules that undergo delayed ionization in region II are detected. Since the drift distance from the point of photon interaction and the grid separating regions I and II is known we can calculate the velocity of the fullerene beams from the onset of the arrival time spectrum. The characteristic beam properties obtained in this fashion are listed in Table 1. The narrowest pulse widths obtained are 20 μs in helium and 70 μs in krypton. The terminal velocity measured corresponds to a fullerene translational energy of 3.6 eV in helium and 700 meV in krypton.

Table 1

PROPERTIES OF SUPERSONIC C_{60} BEAMS IN HELIUM AND KRYPTON

(The C_{60} molecules are nearly fully accelerated to the terminal velocity of the krypton buffer and to approximately 50% of the helium buffer. The corresponding translational energies of C_{60} are 0.7 and 3.6 eV.)

Buffer Gas	V_{term} $(5/2)kT^a$ (10^4 cm/s)	V_{C60} (10^4 cm/s)	E_{trans} (eV)	Pulse Width of C_{60} (μs)
Helium	17.6	9.8	3.6	20
Krypton	4.4	4.3	0.7	70

[a]Calculated terminal velocity at the gas temperature of the buffer gas, T = 300 K.

PHOTOIONIZATION STUDIES

We examined the photoionization of C_{60} using a Nd:YAG laser at the wavelengths of 266 nm and 532 nm, using a picosecond dye laser at 640 and 310 nm, and using an excimer pumped dye laser tunable in the range from 310 to 360 nm. The most detailed work addressed the tunable range from 315 to 335 nm, where a strong one-photon absorption peak is known to occur in the liquid and thin film phase.

Using the cold source, we observed a sharp absorption peak centered on 3.8 eV in C_{60} as shown in Figure 5. Nominally, two photons should be sufficient to reach the ionization limit at C_{60} at this wavelength, but a power dependence of 2.5 was observed in our experiment. The observed power dependence is likely due to the fact that, following one-photon absorption, the excited intermediate relaxes by intramolecular energy transfer to lower lying states of C_{60}, which have an ionization potential larger than the one-photon energy. The power dependence of 2.5 rather than 3 is probably a result of saturation in the second absorption step.

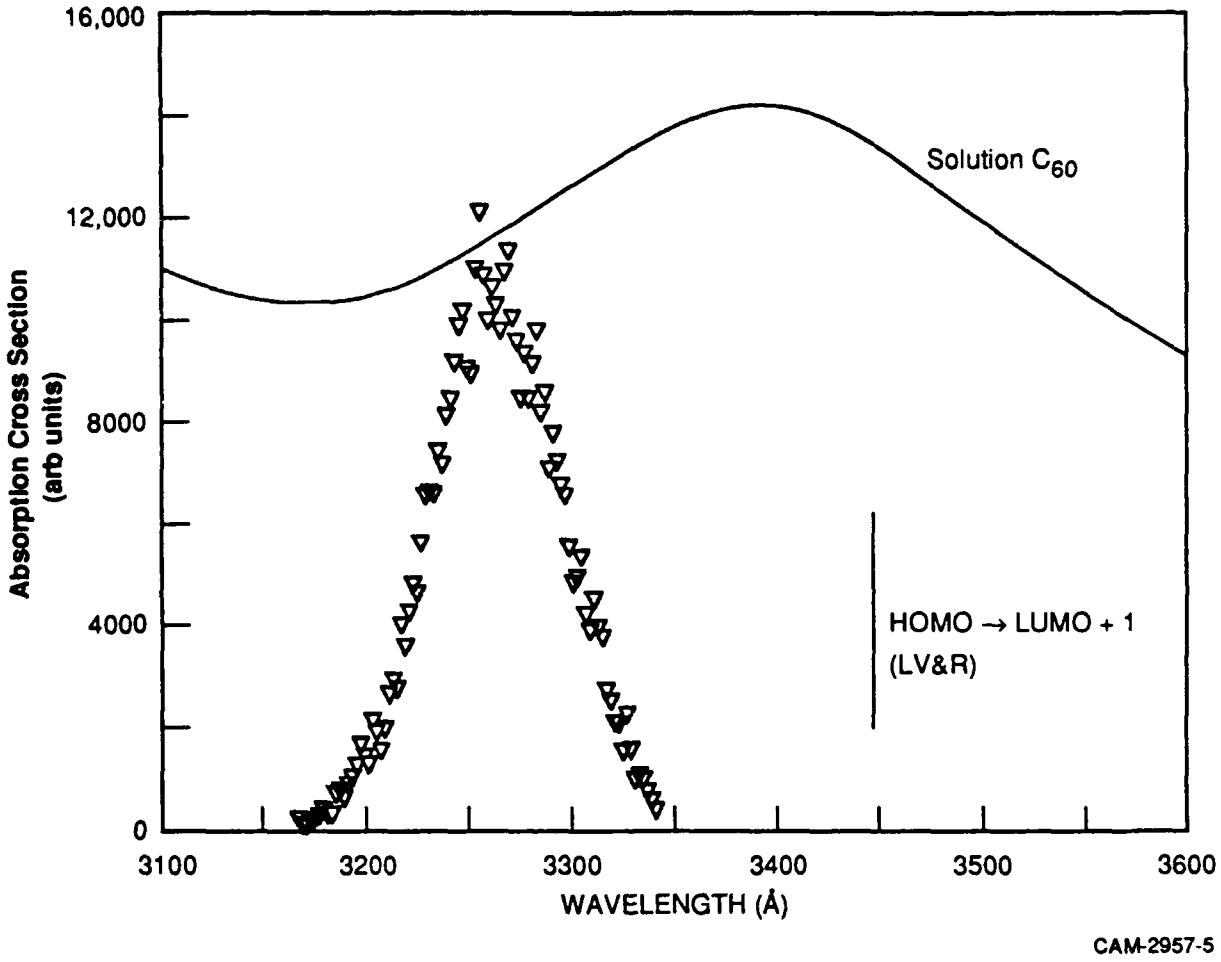


Figure 5. Wavelength dependence of 1 + 1 photon resonant ionization through the lowest energy allowed transition in C_{60}.

The absorption spectrum of a thin film sample of solid C_{60} is shown also. The bar marks the theoretical position of the lowest energy excited state.

In Figure 5 the observed C_{60}^+ signal has been scaled with the power of 2.5 to show the wavelength dependence of the multiphoton ionization cross section. For comparison, we show by the solid line the one-photon absorption cross section of a sample of C_{60} dissolved in toluene. The absorption peak of gas phase C_{60} is shifted to the red by about 50 Å and it is significantly narrower than the liquid sample. The position predicted by theory for the lowest allowed electric dipole transition (HOMO→LUMO+1) is indicated in the figure as well.

PHOTOFRAGMENTATION

Photodissociation studies[1] have shown that the dominant process at moderate intensity is loss of C_2 units. The accepted model for this process[1,2] is elimination of a pentagon-pentagon edge following an initial Stone-Wales isomerization. Stanton[2] calculates the energy required to remove a single C_2 unit from C_{60} to be 13 eV for the neutral and 11 eV for the ion. As a consequence, many photons are required to achieve fragmentation. Figure 6 shows two sample spectra obtained at 328 nm using 15-ns pulses at two intensities. C_2 loss is observed, leading to fullerene molecules with masses as low as C_{32}. Fragmentation to smaller units spaced by units of C is observed at higher intensity.

DELAYED PHOTOIONIZATION

The tailing of the mass peaks in Figure 6 is due to delayed ionization. The mass scale in Figure 6 is obtained by converting the arrival times of ions to carbon mass units and peaks at the respective location refer to ions produced immediately following the photon pulse. When delayed ionization occurs, the conversion of the x-scale leads to apparently higher values of mass. The tailing is particularly pronounced in the case of C_{60}, but it appears also on some of the higher fragment masses. Figure 7 shows in more detail the arrival time spectra obtained from a mixed sample of C_{60} and C_{70} produced from multiphoton absorption. The top spectrum is for excitation by a 20-ns source. The C_{60} and C_{70} peaks are followed by a long tailing signal, which is attributed to delayed ionization.[3] The interpretation of this effect is as follows: C_{60} may absorb many photons and store this excess energy in the form of internal excitation among the many electrons and among the many vibrational degrees of freedom without either ionizing or dissociating. At some later time, the energy stored within one C_{60} molecule may concentrate in a degree of freedom that leads to emission of a photoelectron. In principle, this process is equivalent to vibrational or rotational autoionization in a diatomic molecule, but here more degrees of freedom

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[1]S. C. O'Brien, J. R. Heath, R. F. Curl, and R. E. Smalley, J. Chem. Phys. **88**, 220 (1988).
[2]R. E. Stanton, J. Phys. Chem. **96**, 111 (1992).
[3]P. Wurtz and K. R. Lykke, J. Chem. Phys. **95**, 7008 (1991).

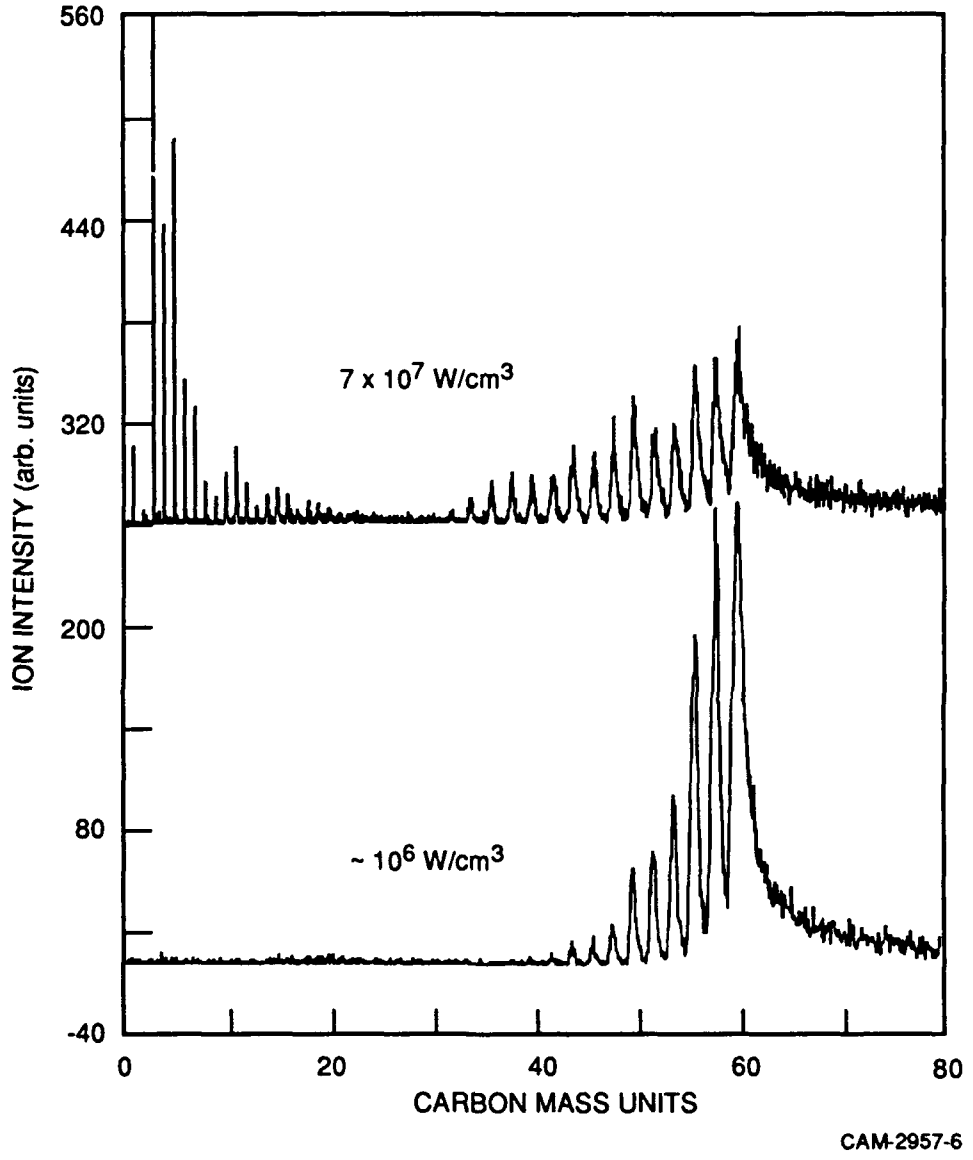

Figure 6. Photoionization, photofragmentation spectrum of C_{60} at two laser intensities at 328 nm.

The tail of the spectrum for C_{60} indicated delayed ionization

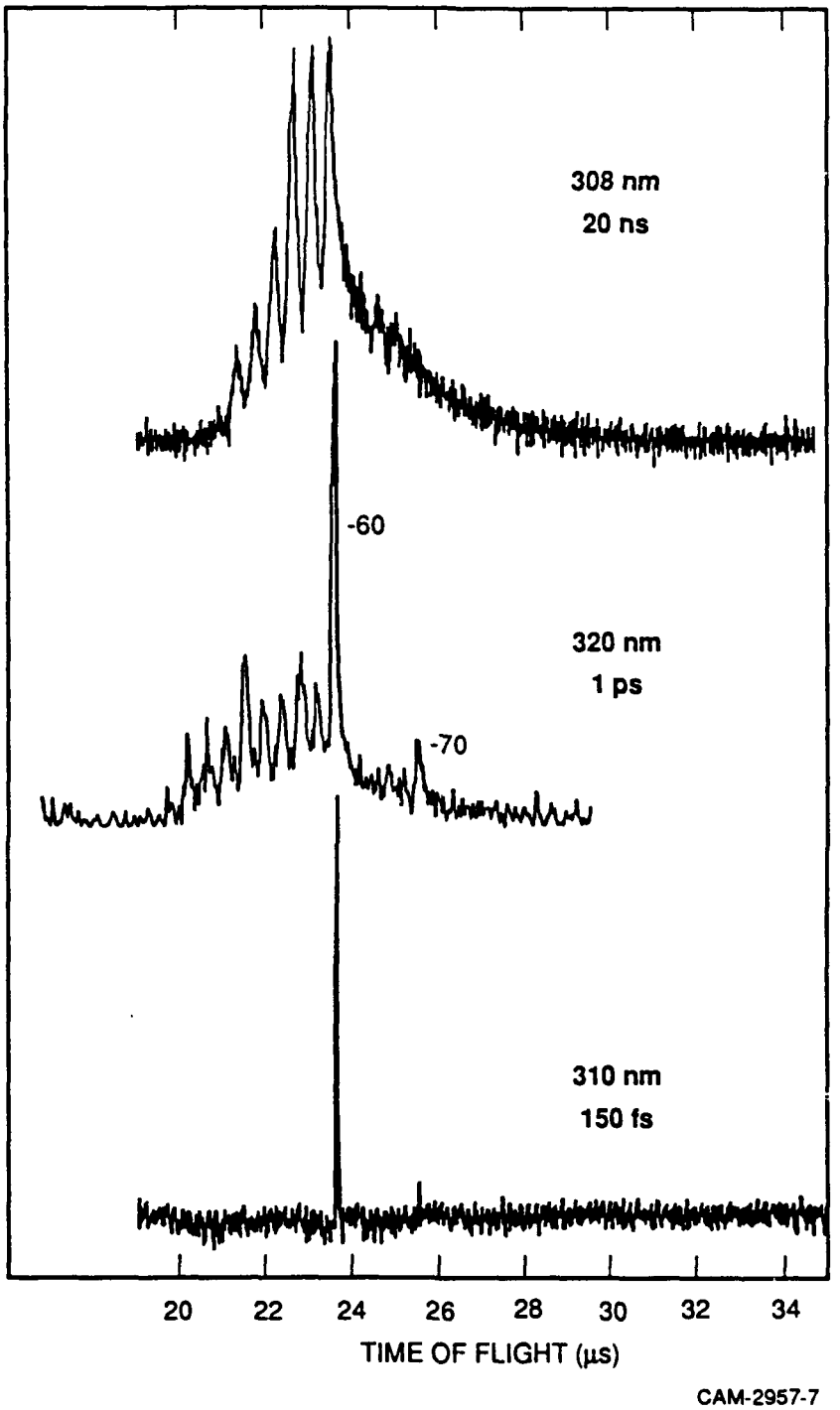

Figure 7. Dependence of delayed photoionization of C_{60}, C_{70} mixture on pulse length.

and more electrons can be simultaneously involved. Wurtz and Lykke[3] recently described this effect as thermionic emission.

The center and bottom curves in Figure 7 show that the contribution from thermionic emission is reduced at shorter pumping times. This observation is consistent with the above discussion. In the limiting case of very short pulse excitation, internal vibrational relaxation cannot compete with vertical transitions of the molecule to the ionization continuum; hence delayed ionization ceases. Since recording these spectra a publication describing similar observations has appeared.[4]

[4]Y. Zhang, M. Späth, W. Krätschmer and M. Stuke, Z. Phys. D. -Atoms, Molecules and Clusters, 23, 195 (1992).

CONCLUSION

An intense supersonic beam source of fullerenes was developed. The properties of the source were characterized using a variety of photoionization techniques. This source does not rely on the formation of fullerenes in the expansion process, but it makes use bulk fullerene material. Its main application is to spectroscopically identify and characterize fullerene molecules under gas phase conditions. An important use of this source is expected for the identification and analysis of endohedral fullerenes (fullerenes doped with atoms or molecules).

PUBLICATIONS AND REPORTS

M. Saeed and H. Helm, "A high temperature pulsed supersonic nozzle source for fullerence beams," in preparation (1992).

D. Schultz, G. Gerber, and H. Helm, "Ultrafast dyanamics of isolated C_{60} and C_{70} molecules," in preparation (1992).

Semiannual report covering the period of 1 January 1992 to 31 July 1992, H. Helm and D. C. Lorents (mail date, 8/25/92).

Semiannual report covering the period of 1 July 1991 to 31 December 1991, H. Helm and D. C. Lorents (mail date, 4/29/92).

PARTICIPATING SCIENTIFIC PERSONNEL

This research was conducted in the Molecular Physics Laboratory by

Dr. D. L. Lorents

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REPORT OF INVENTIONS

There are no inventions to be reported under this contract.